

# Atomistic modeling of diffusion

## Methodology, results and prospects

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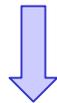
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# What is an atomistic simulation?

- Atomic bonding is described by semi-empirical interatomic potentials (classical force fields)
- Number of atoms  $N = 1-10^6$
- System size 0.5-50 nm (atomic to nano-scale)
- MD time a few nanoseconds (heroic simulations up to a microsecond)
- Bridge between first-principles methods and continuum

## Diffusion simulations:

- Atoms move by a considerable distances
- Statistical averaging over many diffusive events



**Atomistic modeling is the most suitable approach**

# Embedded-atom potentials (EAM)

Potential form:

$$E_{tot} = \sum_i E_i \quad E_i = \frac{1}{2} \sum_{j \neq i} V_{ij}(R_{ij}) + F_i(\bar{\rho}_i) \quad \bar{\rho}_i = \sum_{j \neq i} \rho_j(R_{ij})$$

- Unary system: 3 functions; binary system: 7 functions
- Each potential function parameterized with 3-5 fitting parameters
- **Experimental data:** cohesive energy, lattice parameters, elastic constants, thermal expansion, phonons, vacancy formation energy, SF energy, heat of formation of compounds, etc.
- **First-principles data:** energy-volume relations for several alternative structures, energy along deformation paths (e.g. Bain path), etc.
- Modern trend: first-principles data dominate
- First-principles data improve transferability
- EAM works best for simple and noble metals

**High-quality potentials available:** Cu, Ag, Ni, Al, Cu-Ag, Ni-Al, Ti-Al

**In progress:** Fe-Ni (with angular forces)

# Diffusion in pure metals

## Point defect formation energy:

- Single defect in a supercell with  $N \sim 10^3$  atoms
- $E_f = E_{\text{def}}(N) - E_{\text{perf}}(N)$

## Point defect formation entropy:

- Origin: distortion of atomic vibrations
- Harmonic approximation
- Dynamical matrix  $(3N-3) \times (3N-3) \rightarrow$  normal frequencies  $\{v_i\}$

$$S = -k_B \sum_{i=1}^{3N-3} \ln \frac{h v_i}{k_B T} + 3(N-1)k_B$$

- $S_f = S_{\text{def}}(N) - S_{\text{perf}}(N)$

Point defect concentration:  $c = \exp\left(\frac{S_f}{k_B}\right) \exp\left(-\frac{E_f}{k_B T}\right)$

# Diffusion in pure metals (continued)

Point defect jumps rate within the harmonic Transition State Theory (TST) (Vineyard, 1957)

$$\Gamma = \nu_0 \exp\left(-\frac{\epsilon_m}{k_B T}\right)$$

Attempt frequency:

$$\nu_0 = \frac{\prod_{i=1}^{3N-3} \nu_i}{\prod_{i=1}^{3N-4} \nu_i^*}$$

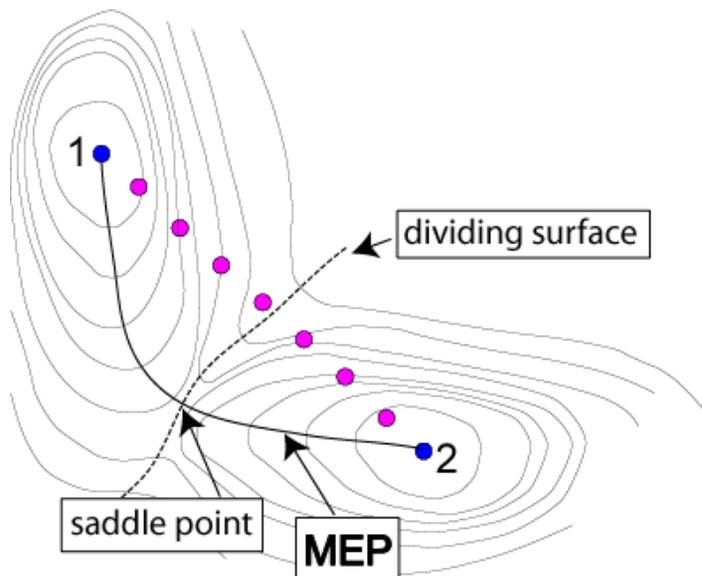
For a vacancy jump – saddle point from lattice symmetry  
Good agreement with experiment for vacancy diffusion in metals  
(e.g. Cu, Ag, Ni, Al)

## Issues:

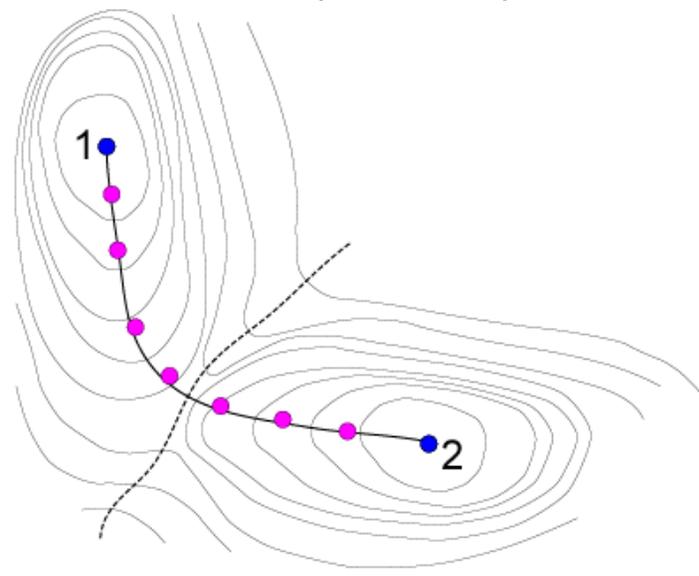
- How to find the saddle point for in more general cases (e.g. interstitial jumps, diffusion in alloys)?
- How to calculate the formation entropy of complex defects?

# Saddle-point search: Nudged elastic band method

Need to know the initial and final states (1 and 2)



Initial band



Relaxed band

$$E_{tot} = \sum_{i=1}^n E(\mathbf{r}_i) + \frac{nS}{2} \sum_{i=1}^n (\mathbf{r}_i - \mathbf{r}_{i-1})^2 \rightarrow \min$$

S – spring constant, n – number of replicas

# Advantages of NEB

- No symmetry required
- Collective jumps are included
- Easy to implement
- Robust and well tested

**Dimer method:** only initial state is needed  
(Henkelmann & Jonsson, 1999)

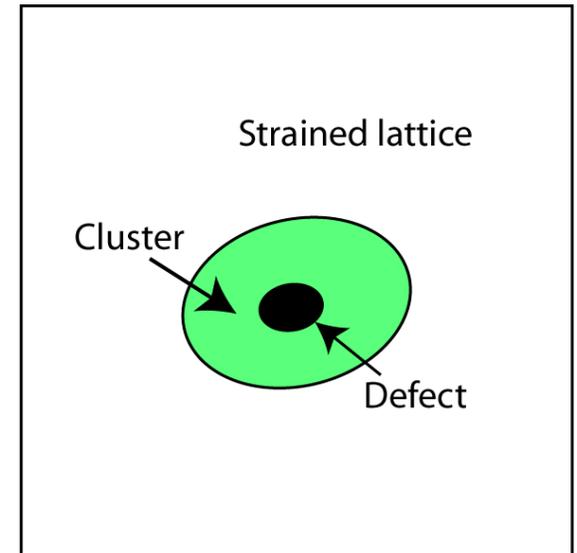
# Defect entropy calculation in large systems

- Relax the large system ( $10^6$  atoms)
- Divide the system in two parts
  - Cluster of dynamic atoms containing the defect
  - Strained lattice regions
- Defect formation entropy:

$$S_f = (S_f)_{\text{cluster}} + S_{\text{elastic}}$$

$S_{\text{cluster}}$  from atomistic harmonic calculations

$S_{\text{elastic}}$  from quasi-continuum calculations



$$\left( \frac{\partial S}{\partial p} \right)_T = -\beta V \implies S_{\text{elastic}} = -\beta \Omega_0 \sum_{i \notin \text{cluster}} p_i \quad \text{where} \quad p_i = -\frac{1}{3} \sum_{\alpha} \sigma_i^{\alpha\alpha}$$

$\beta$  - thermal expansion factor,  $\Omega_0$  - atomic volume,  $\sigma_i^{\alpha\alpha}$  - stress tensor on atom  $i$ .

# Advantages and possible extensions of the embedded-cluster method

- The elastic entropy calculation is a fast linear-N procedure
- Computer time is dominated by the cluster calculation
- Can handle up to millions of atoms

Possible extensions:

- Include second-order invariants of stress
- Include gradient terms,  $(\nabla p)^2$

# Impurity diffusion in metals

FCC metals: five-frequency model

$$D_i = a^2 c f \Gamma_2$$

Correlation factor  $f(\Gamma_0, \Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4)$

Previous work: Adams, Foiles and Wolfer (1989). Entropies and attempt frequencies from empirical correlations

## Procedure:

- $c$  from molecular statics and harmonic approximation
- $\Gamma$ 's from harmonic TST and NEB

**Bottleneck of the calculation: accurate EAM potentials!**

# Diffusion in concentrated alloys

Assume the vacancy mechanism. Consider a binary alloy.

Two computational approaches:

## ■ Molecular dynamics

- Create a vacancy and let it wander through the alloy
- Calculate  $D_A$  and  $D_B$  from mean-squared displacements of atoms
- Impractical in most system

## ■ Kinetic Monte Carlo modeling

- Must know transition rates  $\Gamma_{ij}$  of all jumps  $j$  from every state  $i$ . Create a single vacancy in the block.
- At each step
  - Calculate the residence time at the current site:  $\tau_i = \left( \sum_{j \neq i} \Gamma_{ij} \right)^{-1}$
  - Calculate the transition probabilities  $P_{ij} = \Gamma_{ij} \tau_i$
  - Select transition, implement jump, advance the clock by  $\tau_i$
- After a long run, determine the diffusion coefficient

$$D_x = c \sum_k X_k^2 / 2t$$

- Method is very fast and accurate. Main issue: **how to find the environmentally-dependent  $c$  and transition rates?**

# KMC models: two-frequency model

- Rigid lattice (Ising model)
- Vacancy exchanges with atoms A and B:  $w_A$  and  $w_B$
- Suitable for studying general problems of diffusion kinetics (jump correlations, relation between interdiffusion and self-diffusion, etc.)
- Compatible with Manning's random alloy model
- Quantitative predictions of diffusion coefficients are problematic
- Coupling to atomistic calculations is problematic ( $w_A$  and  $w_B$  actually depend on the environment; how to find the vacancy concentration?, etc.)

# KMC models: Martin's model

- Rigid lattice (Ising model)
- Bragg-Williams model to describe the alloy thermodynamics
- Vacancy formation energy = energy of broken bonds
- TST for vacancy jumps. Vacancy migration barrier

$$\varepsilon_m = \varepsilon_s - \varepsilon_b$$

$\varepsilon_b$  - energy of broken bonds of the jumping atom

$\varepsilon_s$  - saddle point energy

- Postulate that  $\varepsilon_s = \text{const}$  and  $v_0 = \text{const}$ 
  - o 4 coordination shells, mix  $\varepsilon_b$ 's in the initial and final states, use Zener's correlation  $\ln v_0 \propto \varepsilon_m$ , ternary systems (e.g. Ni-Al-Cr), etc.
  - o of diffusion-controlled processes, e.g. phase separation, ordering kinetics, etc. Implementation is simple
  - o quantitative predictions of diffusion coefficients

## KMC models: Martin's model (continued)

- Bragg-Williams model is not state of the art in alloy thermodynamics
- Physical grounds of  $\varepsilon_m = \varepsilon_s - \varepsilon_b$  are not clear
- $\varepsilon_m$  is sensitive to distant neighbors\*
- $\varepsilon_s$  does not work with any reasonable accuracy\*
- Zener's correlation does not work well\*
- Some configurations are mechanically unstable\*

\*J.L. Bocquet (2002), Relaxed EAM simulations for Ni-Au alloys

There was a brief interest in KMC models based on a large rate catalog attempting to enumerate all possible configurations within a few coordination shells around a vacancy. Each rate is obtained by a relaxed calculation.

# On-the-fly KMC (OFKMC) models

Example (J.L. Bocquet, 2002):

- Map the alloy onto a lattice
- Create a vacancy
- At each step:
  - Compute  $\Gamma_{ij}$  (TST + NEB) for each of  $z$  neighbors of the vacancy  
This is a fully relaxed harmonic calculation!
  - Calculate the residence time and jump probabilities
  - Select the jump direction, implement the jump, advance the clock
- Calculate  $D$  from mean-squared displacements of atoms
- Problems
  - The algorithm is extremely slow
  - Some configurations are mechanically unstable and have to be skipped
- Very useful as a testing ground of faster methods

# On-the-fly KMC (OFKMC) models (continued)

Henkelmann and Jonsson (2001):

- No mapping on a lattice
- Escape route is decided by the dimer method
- The escape rates from TST
- The rest of the procedure is the same as before
- The algorithm is still slow
- The method solves the problem of unstable states
- Amorphous and disordered alloys are now tractable
- The method was applied to surface diffusion, island ripening and surface growth
- No applications to bulk diffusion (?)

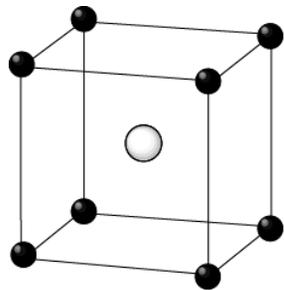
The issue that still remains: **how to calculate the vacancy concentration?**

# Diffusion in ordered compounds

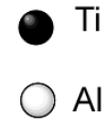
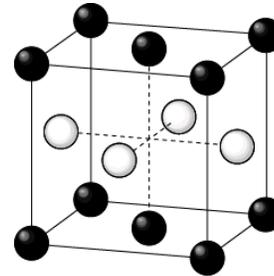
- Multiplicity of point defects and disorder mechanisms
  - Which defects dominate thermal disorder?
  - Which defects accommodate non-stoichiometry?
- Diffusion mechanisms are poorly understood
  - How can vacancies diffuse without destroying the long-range order?
  - Sublattice diffusion *versus* cycles
- Predictive calculations of diffusion coefficients

# Point defects in ordered compounds

Lattice gas model of non-interacting point defects:



**B2 structure**



**L1<sub>0</sub> structure**

Minimize the Gibbs free energy of the defected crystal:

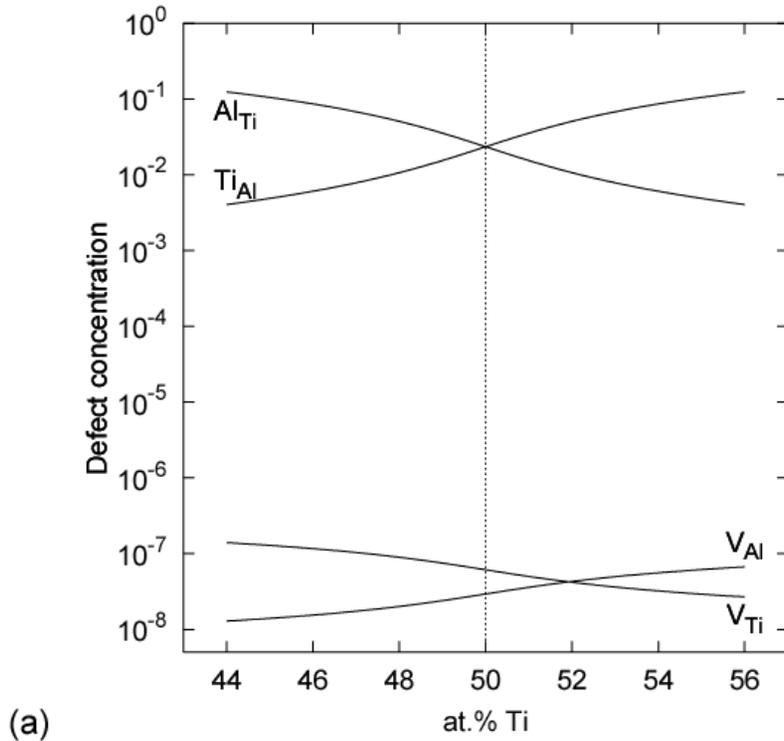
$$G = G_0 + \sum_d c_d \left( \varepsilon_d - TS_d^{\text{vib}} + p\Omega_d \right) - TS_{\text{conf}}$$

For example, in TiAl:  $d = V_{\text{Ti}}, V_{\text{Al}}, \text{Ti}_{\text{Al}}, \text{Al}_{\text{Ti}}$

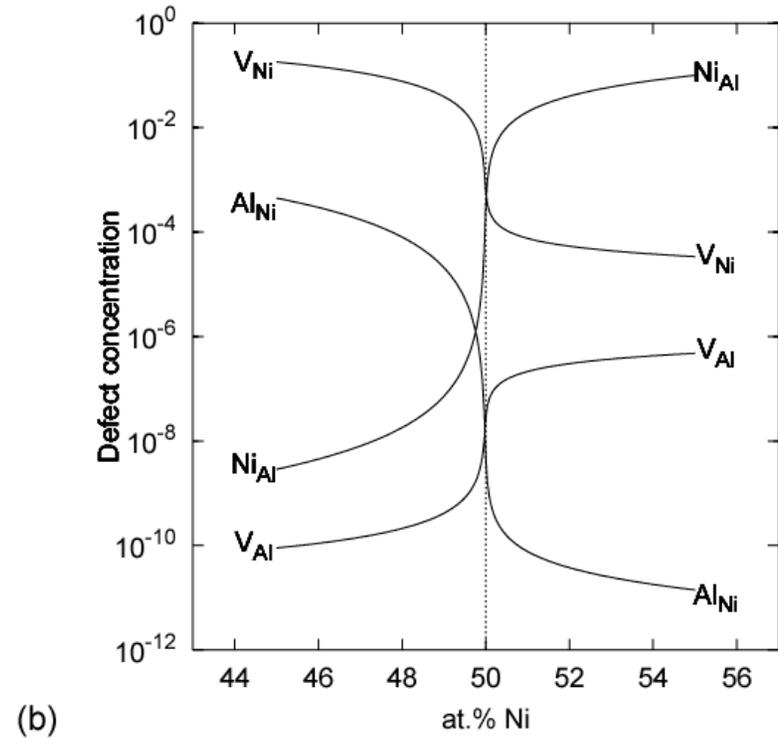
- $\{\varepsilon_d\}$  and  $\{\Omega_d\}$  from molecular statics
- $\{S_d^{\text{vib}}\}$  from harmonic lattice dynamics
- $S_{\text{conf}}$  in the mean-field approximation

$$\Rightarrow \left\{ c_d(T, p, c_{\text{Ti}}) \right\}_{\text{eq}}$$

# Point defect concentrations in TiAl and NiAl



TiAl



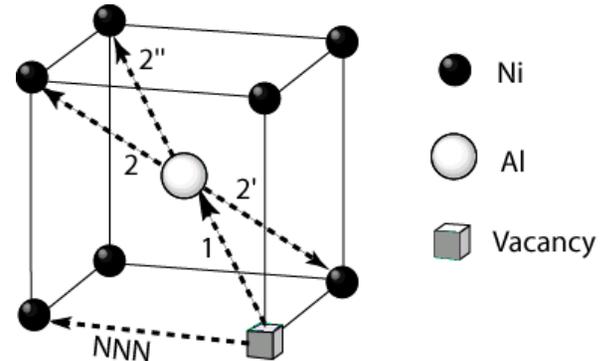
NiAl

**T = 1000 K**

# Diffusion mechanisms in NiAl: NNN vacancy jumps

- Sublattice diffusion by nearest-neighbor vacancy jumps is impossible
- For next-nearest-neighbor (NNN) Ni vacancy jumps, the jump barrier is
  - EAM:  $E_m=2.33$  eV
  - First-principles:  $E_m= 2.48$  eV

- For Al vacancy  $E_m$  is prohibitively high
- Ni diffusion coefficient in stoichiometric NiAl



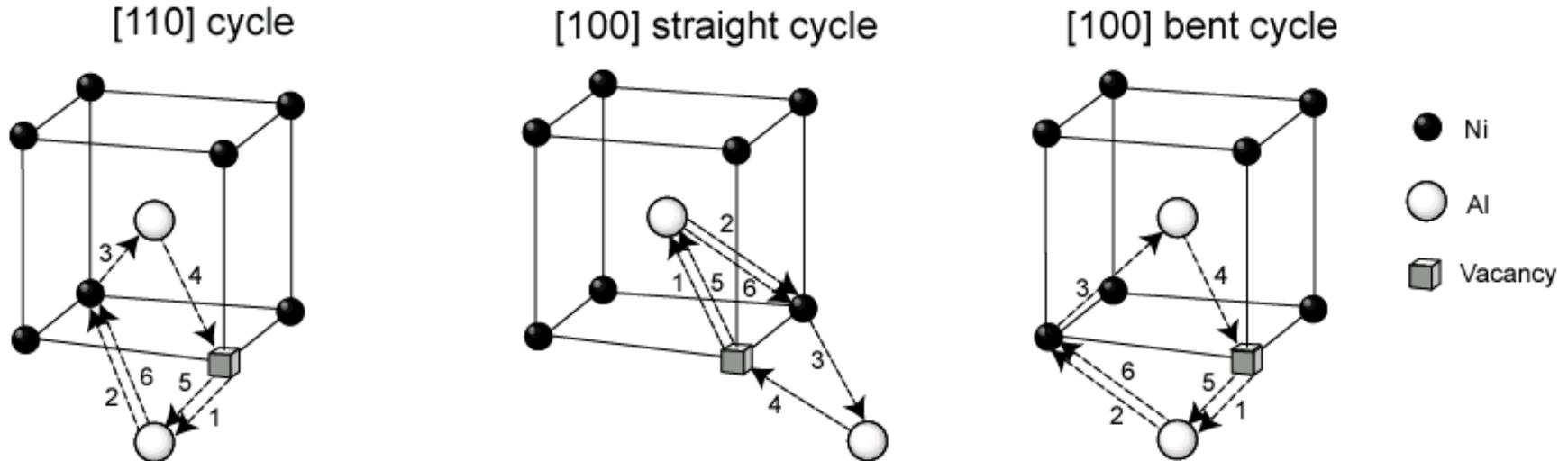
$$D_{\text{Ni}} = a^2 f_0 c_v \Gamma, \quad \text{where} \quad \Gamma = \nu_0 \exp\left(-\frac{E_m}{kT}\right)$$

Activation energy of Ni diffusion:

- Calculated  $Q = 3.09$  eV
- Experimental:  $Q = 3.0$  eV

**NNN jumps can  
contribute to Ni diffusion**

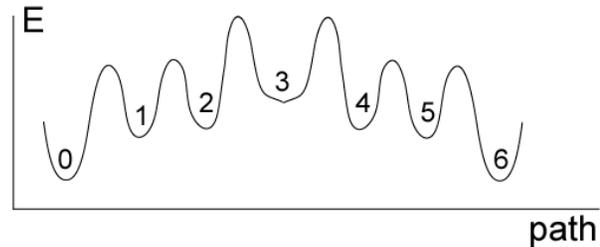
# Diffusion mechanisms in NiAl: six-jump cycles (6JC)



- Highly correlated sequence of 6 vacancy jumps
- Ni vacancy makes a long jump (NNN or NNNN) on the Ni sublattice
- It swaps two Al atoms (NNN or NNNN)
- Order is destroyed during the cycle but is recovered upon its completion
- Ni and Al atoms diffuse simultaneously

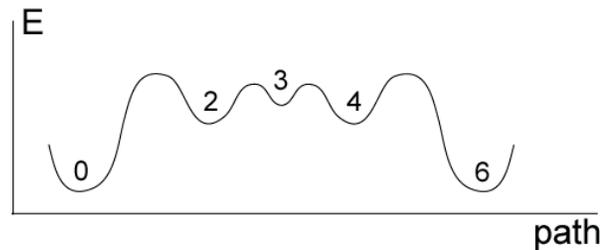
# Collective vacancy jumps in NiAl

Expected:

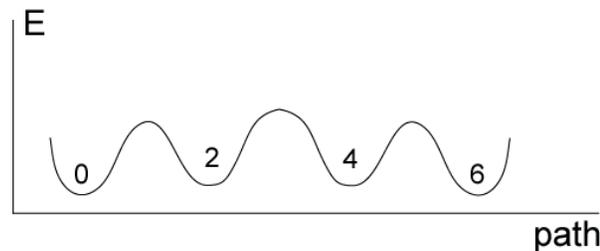


Calculated:

[100] 6JCs



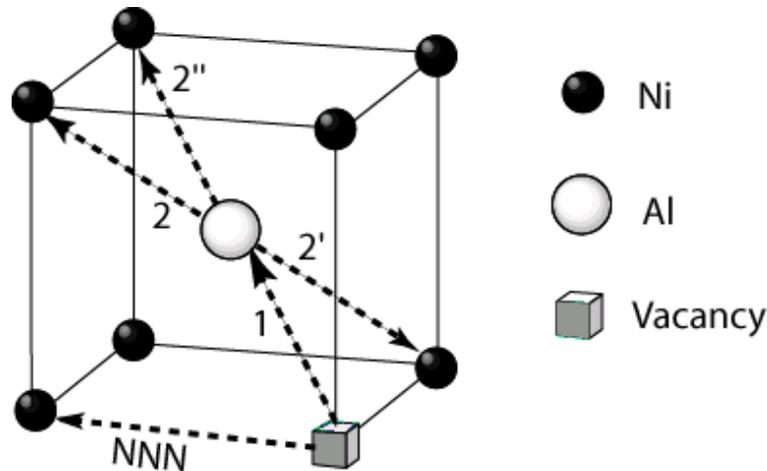
[110] 6JC



6JCs occur by **collective** vacancy jumps

- [110] 6Jcs are most favorable
- $E_m \approx 2.5$  eV

# Unstable vacancies in NiAl



$$1-2 \Rightarrow [110] \text{ 6JC}$$

$$1-2' \Rightarrow [100] \text{ 6JC}$$

Exchange of Ni vacancy with Al (jump 1) atom results in a **mechanically unstable** configuration. Verified by first-principles calculations.

$\Rightarrow$

Jump 1 merges with jump 2 (or 2' or 2'') in one **collective transition**

# Ni vacancy diffusion in NiAl: MD simulation

## Computational challenges:

- Block should be large ( $> 1000$  atoms)
- $E_m \approx 2.5$  eV  $\Rightarrow$  residence time  $\approx 1$ -10 ns at  $T_m = 1940$  K  $\Rightarrow t_{MD} \approx 1$   $\mu$ s

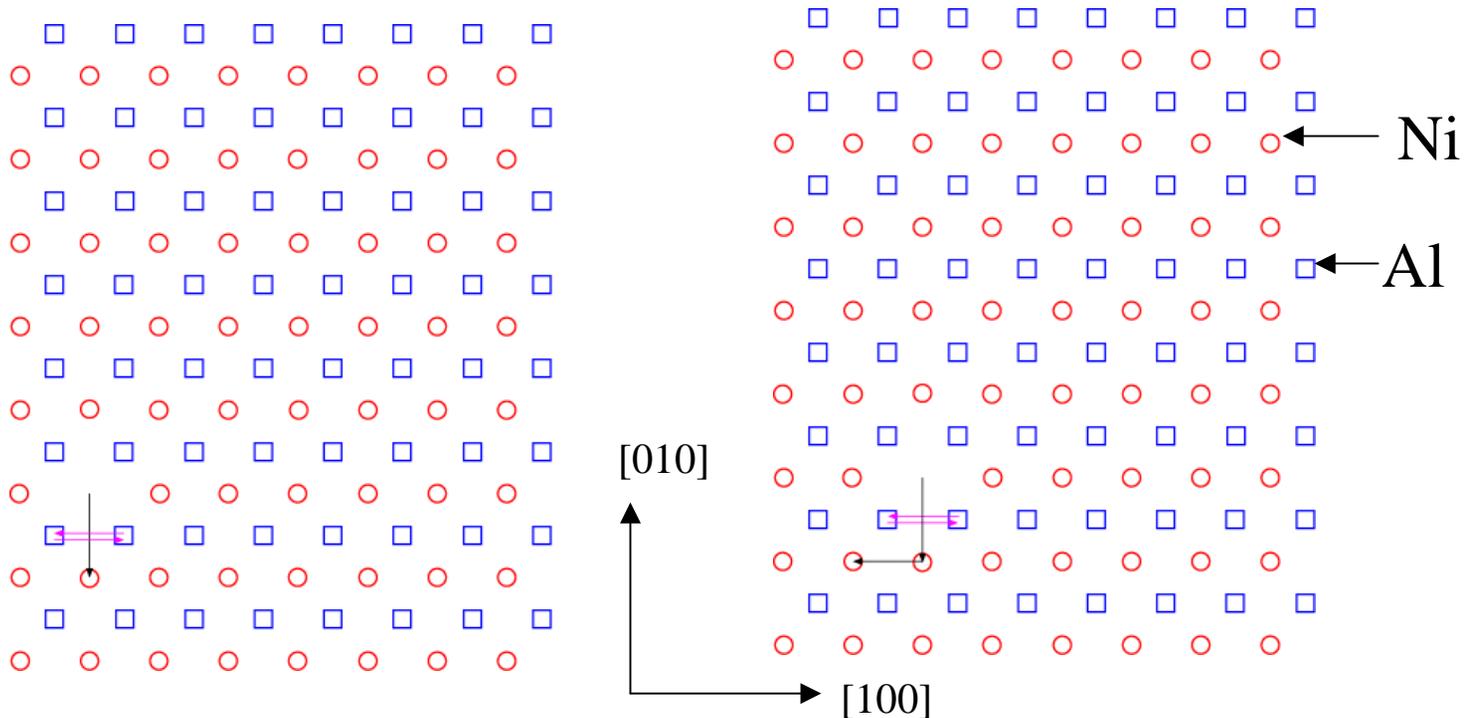
## MD simulation conditions

- 1024 atoms + single Ni vacancy
- $T = 1900$  K
- $t_{MD} \approx 1$   $\mu$ s
- Automated detection of transitions
- Analysis of diffusion mechanisms *a posteriori*

# MD simulation results for NiAl

Events found:

- NNN jumps
- [110] 6JCs
- [111] jumps



# Diffusion mechanisms in NiAl

## Ni diffusion:

- Established
  - NNN vacancy jumps
  - [110] six-jump vacancy cycles
- Unexplored
  - Triple defect mechanism
  - Anti-structural bridges

**Experimental data available**

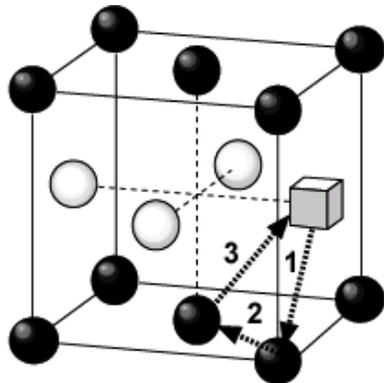
**Al diffusion:** totally unexplored

**Experimental data not available**

# Diffusion mechanisms in TiAl

- Sublattice self-diffusion
- Sublattice antisite diffusion
- Six-jump vacancy cycles (6JC)
- Three-jump vacancy cycles (3JC)

## 3JCs of an Al vacancy:

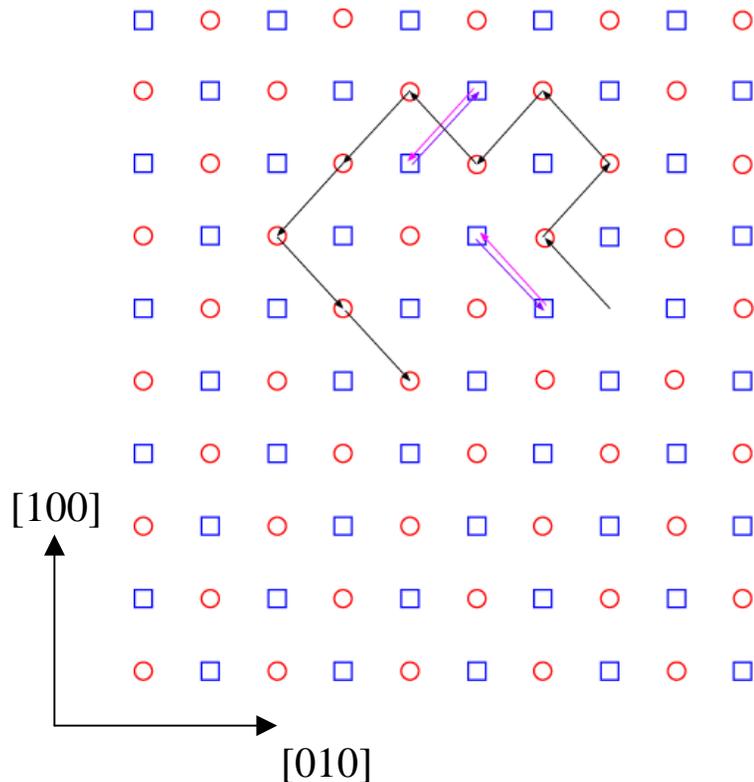


Al vacancies move Ti atoms and vice versa.

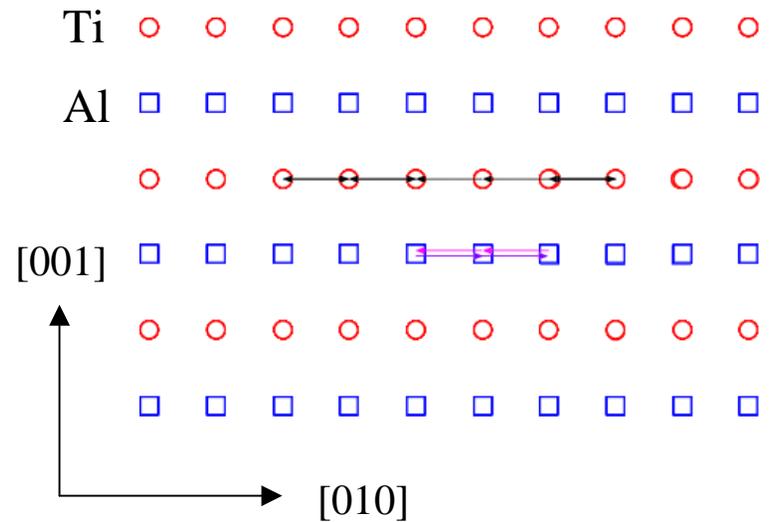
- No NNN jumps
- No unstable vacancies

# MD simulation results for TiAl

- Events found:
- Sublattice self-diffusion (Ti and Al)
  - 3JCs



## MD simulation results at 1000 K:



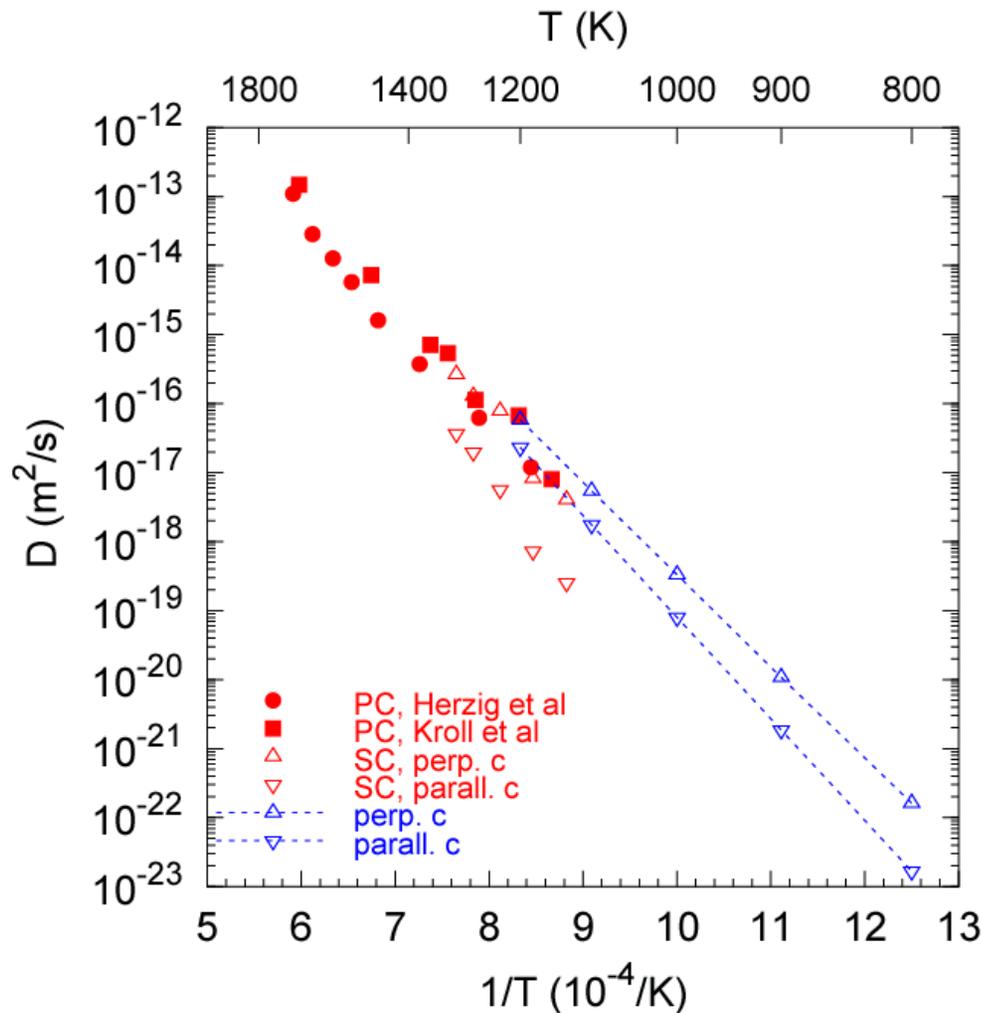
# KMC simulations of diffusion in TiAl

Rate catalog includes:

- Inter-sublattice and intra-sublattice vacancy jumps
- Exchanges with antisites
- Three-jump vacancy cycles

Simulations deliver diffusion coefficients of Ti and Al parallel and normal to the *c*-axis

# Calculations versus experiment



# Summary

- Atomistic simulation is a powerful tool for diffusion calculations
- **Capabilities as of today:**
  - Self-diffusion in pure metals
  - Impurity diffusion in metals
  - Beginning to explore diffusion in ordered compounds
  - Diffusion in disordered alloys is still a big problem
- **Challenges:**
  - Push the time scale of MD
  - Efficient OFKMC schemes
  - Accurate interatomic potentials are needed